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No. 7

~~for~~

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[Development of an "Osmotic Still" and...]

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NEW PRODUCT RESEARCH of TAPCO

Monthly Progress Report No. 7
February 15, 1963

I INTRODUCTION

This document represents the seventh monthly report covering the work on the experimental program for development of an "Osmotic Still" and improvements in the performance characteristics of the Ionics Dual Membrane Fuel Cell during the month of January 1963. This development work is being accomplished under NASA-Lewis Research Center Contract No. NAS 3-2551 by the New Product Research Department of TAPCO and Ionics, Inc. as a subcontractor to TAPCO.

II OVERALL PROGRESS

A. Tapco Portion of Program

1. A total of fourteen (14) successful test runs on the AMF C-60 cation membrane were completed over an electrolyte temperature range from 125°F to 200°F. The maximum water extraction rate obtained at a temperature of 200°F and a vapor pressure of 2.67 psia was 153 cc/hr-ft^2.

2. A total of three (3) successful test runs on the AMF C-103 cation membrane were completed at 125°F. The maximum extraction rate was 39 cc/hr ft^2 at a vapor pressure of 1.41 psia. Tests on this membrane were discontinued due to the low water extraction rate as compared to that achieved with the C-60 membrane.

3. The water extracted from all tests indicated a Ph of four (4) or above using a Taylor Ph meter as the indicator device.

4. Kel-F dispersion was applied to the monel support screens for corrosion resitance and all the above test runs were completed utilizing this initial coating. Periodic inspection of these screens showed little if any corrosion of the monel, and the coating is still in excellent condition.

5. Ionac membranes were ordered, received and prepared for testing during the next reporting period.

B. Ionics Portion of Program

1. Notable progress was made in the areas of materials testing and electrode development. Studies of membrane leakage were carried out. Single-cell studies continued and multiple-cell studies were initiated.

2. Experimental work on the resistance of various materials to chemical attack by 6N H_2SO_4 at 95°C was concluded. Studies were carried out both at Ionics and under subcontract at Arthur D. Little, Inc.

Twenty-one different samples were tested in order to find suitable materials for pusher and separator plates. Of these, 6 samples based on tantalum, niobium and zirconium showed corrosion rates well below the acceptable 8 mils/yr. The titanium-based components that have been used in cells operating at 30°C and 60°C had corrosion rates above 1000 mils/yr. when tested at 95°C.

3. Non-metallics tested included one Ionics and three competitive ion-exchange membranes, 5 materials for possible use as gaskets, 15 for electrolyte and gas compartments and one for use as a mesh-spacer in electrolyte compartments.

Satisfactory resistance was exhibited by the Ionics membrane, two of the gasketings (butyl and Viton-A rubbers), 8 of the compartment or "spacer" materials (Teflon, Kel-F, Penton, Halon-TVS 300, ADM Aropol-7250, Hetron 92, Nypol 4050, Atlac 382) and the Trilok mesh spacer. The Buna-N gasketing and epoxy-fiberglass compartment frame material currently used at 30°C and 60°C did not show acceptable resistance at 95°C.

4. Efforts to prepare electrodes which permit drawing given current densities at higher voltages were continued. Electrodes were tested in small screening cells having 4 sq. in. of ion-exchange membrane on each side of the electrolyte compartment. (These cells were used to speed up the effort during a period where the main test cell rack was plagued by control system malfunction.) Characterization curves of voltage vs. current densities were obtained at ambient temperature. Tests at Ionics dealt primarily with electrodes separate from the membrane; the subcontracted work at Arthur D. Little deals with electrodes prepared integrally upon the membrane.

Six different types of separate electrodes were tested. Sintered electrodes using teflon dispersion and Pt black were found to be best. Further studies pinpointed the optimum amounts of teflon for the hydrogen and for the oxygen electrodes. Results from the subcontracted work on integral electrodes are not available as yet.

5. Small, 4 sq. in. test cells showed that at least under "ideal" gasketing and hydrostatic head conditions, no appreciable amounts of liquid pass through the membrane.

6. No signfficant difference was found in the initial performance of 36 sq. in. cells whether operating at 30°C or 60°C, 5 psig or 16 psig. Effects of variations in electrode and membrane type were clouded by the appearance of sizeable amounts of liquid in the gas compartments and several control system failures.

7. Successful cell performance was demonstrated by maintaining 16 amps/ft^2 at more than 0.8 volts for 72 hours until shut-down by control system malfunction. (Design goal corresponds to 100 hours at 16 amps/ft^2 and 0.76 volts.)

8. Multiple cell battery design has been initiated, materials ordered and partially received.

III CURRENT PROBLEMS

A. Tapco Portion of Program

1. Several delays in test completion have occurred due to hose rupture in the parastaltic pump. The repetitive flexing of the hypalon hose used in the pump caused hose failure and acid spilling with a few hours of operation. However, the adjustment of the flexing pressure on the hose and the addition of parallel hoses in the pump (which permitted a reduced pump speed without a flow rate reduction) has eliminated this problem.

2. Upon "Still" startup, a cleanup period, as reported in the last monthly report, is required for the extracted water Ph to raise from one (1) to above four (4). During the initial tests with the parastaltic pump installed in the test rig, a cleanup could not be obtained. Upon disassembly of the test unit, it was found that one of the two membranes was sweating and the other was not. Leak tests with a cationic dye applied to the membrane indicated no leakage in the membrane. Further tests indicated a large flow maldistribution in the two acid cavities of the test unit causing condensation on one membrane. Buildup of this condensation caused liquid runoff into the condenser. This flow maldistribution

was caused by the inability of the parastaltic pump (due to a reduced flow capacity) to purge the air out of one of the upper acid exit lines. This condition was corrected by increasing the pump flow rate and by a minor modification of the test rig. Also, thermometers have been mounted at both acid exits from the still for continuous monoritoring to detect flow maldistribution if it occurs. After elimination of this problem, testing continued at a rapid rate without failure.

B. Ionics Portion of Program

1. The control system for testing single and multiple cell batteries needs revamping.

2. Delivery of ordered materials needs additional expediting.

IV NEXT MONTH'S EFFORT

A. Tapco Portion of Program

1. Initiate performance test of the Ionac membranes.

2. Procure and test available non-wetting, porous materials.

3. Select most promising membrane based on test results obtained in the test unit still and complete the detailed performance testing of that membrane.

B. Ionics Portion of Program

1. Revamp control system on cell test racks to eliminate frequent early test shut-downs.

2. Conclude small-cell electrode development and membrane leakage tests.

3. Firm-up design of all major components for 5-cell battery on best current electrodes, membranes and materials.

4. Expedite receipt of ordered materials.

5. Fabricate all major components for two 5-cell batteries.

V TEST RESULTS

A. Tapco Portion of Program

1. Kel-F dispersion KX-633 was applied to the monel metal support screens for corrosion resistance. The screens were dipped in full strength dispersion and the excess was blown off with an argon gas stream. The solution was allowed to

air dry and then was placed in a 500°F oven for 20 minutes. Three coatins were applied in this manner. All the test runs during this reporting period were made with these screens as supports and visual observation at the end of this period revealed only a slight discoloration in the metal in a few spots beneath the coating. The coating, however, is still in tact and appears to be in excellent condition.

2. Attached to this report is a plot of reduced test data obtained up to and through this reporting period (see TRW Figure 1A). The plotted data includes tests from three types of AMF membranes, A-60 anion, C-60 cation, and C-103 cation; all with 30% acid solution. The data is plotted with water extraction rate versus the vapor pressure difference between the vapor pressure of the 30% acid solution at the given temperature and the vapor pressure maintained in the test unit. The data is presented in this manner to permit a correlation that includes all of the pertinent test variables such as acid temperature, acid concentration and test unit vapor pressure. The plotted data indicates that for a given membrane, the extraction rate is a function only of vapor pressure difference.

3. Attached to this report is the raw laboratory test data taken during this reporting period.

B. Ionics Portion of Program

1. Materials Testing

Tests were carried out at Arthur D. Little and at Ionics. Results are shown in Tables I, II, III, and IV.

At present the most promising materials are:

Membrane:	Ionics' 8 oz. glass backed
Insulator Sheets:	Butyl rubber
Gasketing:	Viton-A
Compartment Frames:	Penton or Halon
Pusher Plates and Separators:	Tantalum
Spacer Mesh:	Trilok

2. Electrode Development

The following electrodes were compared:

i. Pt-Rh gauge sprayed with Pt black and polyethylene solution in benzene.

ii. Sintered electrodes using 0.28 gm Kel-F dispersion, 0.4 gm MgO and 4.0 gm Pt black for two 2" x 2" electrodes.

iii. Sintered electrodes using 0.28 gm Kel-F dispersion and 4.0 gm Pt black per pair.

iv. Pt-Rh gauge electrolytically coated with Pt.

v. Sintered electrodes fabricated by Clevite Corporation using 4.0 gm Pt black, 0.24 gm teflon dispersion and 0.4 gm MgO.

vi. Sintered electrodes as in (v) but without MgO.

Detailed characterization curve data are given in Figure 1. Sintered electrodes using teflon prepared according to (vi) above gave the best results: 0.73 volts at the standard current density of 16 amps/ft^2. It should be noted that the performance of the electrodes prepared by Clevite according to Ionics' instructions gave almost the same results as sintered electrodes of the same composition prepared at Ionics.

To further optimize electrode performance, sintered electrodes were prepared using 0.13, 0.52, 1.07 and 2.0 gms of teflon per cell, corresponding to 0.0025, 0.01, 0.02 and 0.04 gms/cm^2. (Figure 2) Half-cell tests showed that 0.0025 gm/cm^2 was the best for the H_2 electrode and 0.020 gm/cm^2 was the best for the O_2 electrode (Figure 3). A composite cell using these two different electrodes gave the expected improved performance: 0.76 volts at 16 amps/ft^2 (Figure 4). The different teflon requirements for the two electrodes could be explained on the basis that the greater wet proofing on the O_2 side helps to prevent the drowning of the catalyst as a result of water formation, whereas on the H_2 side, since no water is formed, the less the amount of teflon, the better it is.

Several additional sintered electrodes are being prepared by Mott Metallurgical Company and will be tested when available.

Some integral electrodes were prepared at Ionics but showed no noticeable advantage over separate electrodes. Work at Arthur D. Little has been initiated and the test results should be available soon.

3. Membrane Leakage

Several of the large 36 sq. in. cells have appeared to suffer from an inordinate amount of liquid appearing in the gas compartments of the cells. Some small 4 sq. in. cells were set up to measure the amount of liquid appearing in the gas compartments under "ideal" conditions, i.e., at ambient temperature, with only a small hydrostatic head pressure differential between electrolyte and gas compartments and with excellent gasketing. The gases were bubbled through electrolyte solution, entered the gas compartments and left through outlets in the bottom of the gas compartment frames. Any liquid carried out was collected in small graduates. A current of 16 ma/cm^2 was drawn from the cell throughout the test.

A test of a cell containing standard 8-oz. cation membranes resulted in approximately .01 to .03 ml/cm^2-day of liquid collected on the O_2 side and just barely noticeable quantities on the H_2 side. These rates can be compared to the 0.13 ml/cm^2-day of just the electrolytically produced water at the current density used. Either evaporation losses or reverse transfer of water into the electrolyte compartment must account for the low water collection rate. Certainly no "leakage" across the membrane into the gas compartments occurred under the conditions of the test.

Tests for membrane leakage at higher temperature and under some slightly higher pressure differential will be carried out in the large 36 sq. in. cells. Some additional membranes will be tested in the 4 sq. in. cells.

4. Single 36 sq. in. - Cell Studies

Extended tests of single 36 sq. in.-cells were carried out to help evaluate the effects of temperature, pusher plate designs, electrode preparation, and pressure level. Many of the tests were somewhat clouded by the appearance of sizeable quantities of liquid in the gas compartments and several failures of the control system. Detailed voltage/current density data are given in Table V.

4.1 Effect of Temperature

Cell E 1282 was run at 60°C and the otherwise identical cell E 1290 was run at 30°C. For the first 100 hours, there was no significant difference between them, both delivering 4.0 amperes at about 0.77 volts. A control system failure interrupted the test at about 100 hours.

4.2 Effect of Pusher Plate Design

Cells D9749 and D9750 were identical except that cell D9750 contained pieces of platinized expanded titanium between the pusher plates and the electrodes. A continuous current of 4.0 amps was drawn from each cell. The output voltage of Cell D9749 (without the expanded metal inserts) dropped below 0.5 volts in about 130 hours. Cell D 9750 (with inserts) maintained its voltage above 0.5 volt until shut down by a control system failure after 432 hours. The expanded metal inserts may have prolonged cell performance by keeping the pusher plates from occluding a good part of the electrode surface.

4.3 Effect of Pressure

Cells 1282 and 1268 were effectively identical except that Cell 1282 was run at 5 psig while Cell 1268 (along with the other cells tested) was run at 16 psig. The initial performance of the higher pressure cell was slightly better but it maintained the advantage for less than a day.

EFFECT OF PRESSURE

HOURS	OUTPUT VOLTAGE AT 16 AMPS/FT^2	
	16 psig	5 psig
5	0.790	0.772
24	0.758	0.782
48	0.698	0.761
96	0.672	0.755
120	0.632	0.740

4.4 Effect of Electrode and Membrane Types

Attempted comparisons between paste and sintered electrodes, standard and tighter membranes Kel-F and teflon sintering aids were not successful as early control system failures or excess liquid accumulation in the gas compartments precluded obtaining significant comparisons.

4.5 Excellent Performance Possible

One of the test cells showed that a dual membrane fuel cell can give excellent performance. The standard current of 4.0 amperes was maintained at more than 0.8 volts for 72 hours.

The polarization curves taken after four hours of operation are shown in Figure 5. The design goal of 0.68 volts at 6 amperes is safely exceeded. The requirement of 100-hour operation should be achievable when control system difficulties and liquid leakages (probably due to poor control system operation leading to undue pressure imbalances) are overcome.

Further immediate efforts on single-cell studies will concentrate on preventing control system malfunctions.

5. Multiple 36 sq. in.-Cell Studies

Two main alternative designs have been outlined:

(a) extension of our present single cell design,

(b) a "back-to-back" configuration in which one gas space serves two electrode surfaces.

The present opinion is that employing the new corrosion-resistant materials suggested by the materials testing program, the present single cell design could be made into a workable 10-cell battery. Materials have been ordered, and some received, to permit the construction of two 5-cell stacks in this design.

The back-to-back configuration, which has several inherent advantages, depends on bringing out from each cell a leakproof electrical connection. Some electrodes to test this idea are in course of preparation at the Cabot Corporation, Cambridge, moulding the platinum screen electrode into a frame of silicone rubber. It is expected that this type of electrode could be self-gasketing.

VI QUALITY ASSURANCE

A. Tapco Portion of Program

The Quality Assurance Status of the program at both TAPCO and Ionics is considered to be satisfactory as it relates to the test activity carried out during this reporting period.

VII MANPOWER CHANGES

A. Ionics Portion of Program

Wayne A. McRae, Vice President, Research - Mr. McRae has taken over the general responsibility for the project. He is spending 15% of his time on the contract.

Werner Glass, Assistant Director, Research - Dr. Glass will assist Mr. McRae in the technical direction of the project. He will devote 60% of his time to the contract.

Test Results Through 1/31/63 - T.R.I.

OSMOTIC STILL TEST RESULTS

Water Extraction Rate
V3
Vapor Pressure Difference

Test Conditions

H_2SO_4 Solution @ 30% concentration

Notation

ΔP = Vapor pressure difference between H_2SO_4 solution Vapor pressure @ temperature and the test vapor pressure, psi

- △ = AMF c-60 @ 200°F
- ○ = AMF c-60 @ 175°F
- □ = AMF c-60 @ 150°F
- ◇ = AMF c-60 @ 125°F
- ▲ = AMF c-120 @ 175°F
- ◆ = AMF A-60 @ 175°F

Water Extraction Rate, gal/sq ft/day

180
160
140
120
100
80
60
40
20
0

0 1 2 3 4 5 6 7

Vapor Pressure Difference △P, psi

TRW Figure 1A